

U.S. Application No.: 10/689,221
AMENDMENT A

Attorney Docket: 3975.025

IN THE CLAIMS:

This listing of the claims will replace all prior versions, and listings, of claims in the application:

1. (currently amended) A powder mixture for resorbable calcium phosphate biocements, characterized by a fraction mixture consisting of (relative to the total volume of the powder mixture):

40-99% by volume of powder having a particle size of 0.1-10 μ m

1-20% by volume of powder having a particle size of 10-43 μ m

0-59% by volume of powder having a particle size of 43-315 μ m

which powder is obtained by grinding the spontaneously crystallizing melts of a material comprising crystalline and X-ray amorphous phases, which material

a) according to ^{31}P -NMR measurements, contains Q_0 -groups of orthophosphate and Q_1 -groups of diphosphate, the orthophosphates or Q_0 -groups making up 65 to 99.9% by weight relative to the total phosphorus content of the powder mixture and the diphosphates or Q_1 -groups making up 0.1 to 35% by weight relative to the total phosphorus content of the powder mixture, and

b) according to X-ray diffractometric measurements and relative to the total weight of the powder mixture, contains 35 to 99.9% by weight of a main crystal phase selected from the group consisting of $\text{Ca}_2\text{K}_{1-x}\text{Na}_{1+x}(\text{PO}_4)_2$, where $x = 0.1$ to 0.9 , $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$, $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$, mixtures thereof and mixed crystals according to the general formula $\text{Ca}_{10}\text{K}_x\text{Na}_{1-x}(\text{PO}_4)_7$, where $x = 0$ to 1 , and 0.1 to 20% by weight of a substance selected from the group consisting of $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{K}_2\text{CaP}_2\text{O}_7$, $\text{Ca}_2\text{P}_2\text{O}_7$, NaPO_3 , KPO_3 and mixtures thereof as a secondary crystal phase, and

c) besides the main crystal phase, contains an X-ray amorphous phase which in total makes up 0.1 to 65% by weight relative to the total weight of the powder mixture

and which material is prepared by combining the substances 30-55% by weight CaO, 35-50% by weight P_2O_5 , 1-20% by weight Na_2O , 0.5-20% by weight K_2O and 0.1-5% by weight
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MgO and optionally up to 5% by weight SiO₂, homogenizing and drying the mixture and subjecting it to a step-by-step thermal treatment lasting 1-2h at 350-450°C, 750-850°C and 950-1,050°C respectively, melting the mixture at between 1,550 and 1,650°C, holding it at the melting temperature for between 10 and 60 minutes and finally cooling the mixture in a spontaneous or temperature-controlled manner and grinding it.

2. (previously presented) A powder mixture according to Claim 1, wherein said mixture contains 0.1-15% by weight, preferably 0.5-4% by weight chain phosphates selected from among NaPO₃, KPO₃, mixed crystals thereof and mixtures of the foregoing, which are indicated by Q₂-groups in ³¹P-NMR measurements.
3. (previously presented) A powder mixture according to Claim 1, wherein the ortho-phosphates make up 40 to 95% by weight.
4. (previously presented) A powder mixture according to Claim 3, wherein the ortho-phosphates make up 50 to 90% by weight.
5. (previously presented) A powder mixture according to Claim 1, wherein the diphosphates make up 1 to 22% by weight, preferably 5 to 22% by weight.
6. (previously presented) A powder mixture according to Claim 5, wherein the diphosphates make up 5 to 22% by weight.
7. (previously presented) A powder mixture according to Claim 1, wherein in the melted or ground state said mixture consists of (in % by weight):

30 to 55 P₂O₅

25 to 50 CaO

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1 to 20 Na_2O
0.5 to 20 K_2O
0.1 to 13 MgO
0.0 to 10 SiO_2

MgO or SiO_2 or a mixture thereof making up at least 1% by weight, and the corresponding crystal phases.

8. (previously presented) A powder mixture according to Claim 1, wherein said mixture contains up to 10% of a silicate phase.
9. (previously presented) A powder mixture according to Claim 1, wherein said mixture additionally contains up to 30% by weight alpha-tricalcium phosphate, beta-tricalcium phosphate or mixtures thereof besides the powder obtained by a melting process.
10. (previously presented) A powder mixture according to Claim 1, wherein said mixture additionally contains an active agent selected from the group consisting of antibiotics, other pharmaceutical active agents, disinfectants, bacteriostats and mixtures thereof.
11. (previously presented) A powder mixture according to Claim 1, wherein said mixture is provided in the form of an aqueous solution, a suspension or a paste.
12. (previously presented) A powder mixture according to Claim 1, wherein in mixed crystals the element Ca is replaced by Mg in an amount ranging up to 20% by weight relative to the weight of the powder mixture.

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13. (previously presented) A powder mixture according to Claim 1, wherein said mixture is provided in a two-component kit wherein one component is said powder and the other component is made up of a water phase.

14. (Withdrawn) A method for manufacturing resorbable calcium phosphate biocements which contain less than 20% by weight hydroxyapatite (HA) and/or precipitated hydroxyapatite besides their initial main crystal phases once the setting process of the cement is finished, said method comprising:

grinding the spontaneously crystallizing melts of a material comprising crystalline and X-ray amorphous phases, which material

a) according to ^{31}P -NMR measurements, contains Q_0 -groups of orthophosphate and Q_1 -groups of diphosphate, the orthophosphates or Q_0 -groups making up 65 to 99.9% by weight relative to the total phosphorus content of the powder mixture and the diphosphates or Q_1 -groups making up 0.1 to 35% by weight relative to the total phosphorus content of the powder mixture, and

b) according to X-ray diffractometric measurements and relative to the total weight of the powder mixture, contains 35 to 99.9% by weight of a main crystal phase selected from the group consisting of $\text{Ca}_2\text{K}_{1-x}\text{Na}_{1+x}(\text{PO}_4)_2$, where $x = 0.1$ to 0.9 , $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$, $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$, mixtures thereof and mixed crystals according to the general formula $\text{Ca}_{10}\text{K}_x\text{Na}_{1-x}(\text{PO}_4)_7$, where $x = 0$ to 1 , and 0.1 to 20% by weight of a substance selected from the group consisting of $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{K}_2\text{CaP}_2\text{O}_7$, $\text{Ca}_2\text{P}_2\text{O}_7$, NaPO_3 , KPO_3 and mixtures thereof as a secondary crystal phase, and

c) besides the main crystal phase, contains an X-ray amorphous phase which in total makes up 0.1 to 65% by weight relative to the total weight of the powder mixture

to thereby form a cement powder with a fraction mixture consisting of (relative to the total volume of the powder mixture):

40-99% by volume of powder having a particle size of 0.1-10 μm

1-20% by volume of powder having a particle size of 10-43 μm

0-59% by volume of powder having a particle size of 43-315 μm

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and which material is prepared by combining the substances 30-55% by weight CaO, 35-50% by weight P₂O₅, 1-20% by weight Na₂O, 0.5-20% by weight K₂O and 0.1-5% by weight MgO and optionally up to 5% by weight SiO₂, homogenizing and drying the mixture and subjecting it to a step-by-step thermal treatment lasting 1-2h at 350-450°C, 750-850°C and 950-1,050°C respectively, melting the mixture at between 1,550 and 1,650°C, holding it at the melting temperature for between 10 and 60 minutes and finally cooling the mixture in a spontaneous or temperature-controlled manner and grinding it.

15. (Withdrawn) The method according to Claim 14, comprising mixing the cement a powder with pure water or aqueous solutions.

16. (Withdrawn) The method according to Claim 15, wherein the setting process takes place using aqueous solutions additionally containing cations, particularly sodium and potassium, and anions, particularly chlorides.

17. (Withdrawn) The method according to Claim 16, wherein cohesion promoters and/or setting accelerators are added to the aqueous solution.

18. (Withdrawn) The method according to Claim 17, wherein at least one compound selected from the group consisting of hydroxyethyl starch, soluble starch, cyclodextrins, alginates, dextran sulphates, polyvinylpyrrolidone and/or hyaluronic acid are selected as cohesion promoters and disodium hydrogen phosphate is added to the aqueous solution as a setting accelerator.

19. (Withdrawn) The method according to Claim 16, wherein the aqueous solution is mixed with the cement powder at a ratio ranging between 0.15 and 0.4ml/g, preferably 0.18 and 0.23ml/g.

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20. (Withdrawn) The method according to Claim 14, wherein said resorbable calcium phosphate biocement is provided in the form of an aqueous solution, a suspension or a paste for manufacturing a biodegradable bone replacement material which can be used both for filling defects in vivo and for cultivating cells in vitro in tissue engineering.

21. (Withdrawn) A biodegradable implant having an open-pore or closed-pore structure, which implant is manufactured using a mixture which is provided in the form of an aqueous solution, a suspension or a paste and has set ex vivo, wherein said mixture is based on a powder mixture for resorbable calcium phosphate biocements, characterized by a fraction mixture consisting of (relative to the total volume of the powder mixture):

40-99% by volume of powder having a particle size of 0.1-10 μ m

1-20% by volume of powder having a particle size of 10-43 μ m

0-59% by volume of powder having a particle size of 43-315 μ m

which powder is obtained by grinding the spontaneously crystallizing melts of a material comprising crystalline and X-ray amorphous phases, which material

a) according to ^{31}P -NMR measurements, contains Q_0 -groups of orthophosphate and Q_1 -groups of diphosphate, the orthophosphates or Q_0 -groups making up 65 to 99.9% by weight relative to the total phosphorus content of the powder mixture and the diphosphates or Q_1 -groups making up 0.1 to 35% by weight relative to the total phosphorus content of the powder mixture, and

b) according to X-ray diffractometric measurements and relative to the total weight of the powder mixture, contains 35 to 99.9% by weight of a main crystal phase selected from the group consisting of $\text{Ca}_2\text{K}_{1-x}\text{Na}_{1+x}(\text{PO}_4)_2$, where $x = 0.1$ to 0.9 , $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$, $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$, mixtures thereof and mixed crystals according to the general formula $\text{Ca}_{10}\text{K}_x\text{Na}_{1-x}(\text{PO}_4)_7$, where $x = 0$ to 1 , and 0.1 to 20% by weight of a substance selected from the group consisting of $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{K}_2\text{CaP}_2\text{O}_7$, $\text{Ca}_2\text{P}_2\text{O}_7$, NaPO_3 , KPO_3 and mixtures thereof as a secondary crystal phase, and

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c) besides the main crystal phase, contains an X-ray amorphous phase which in total makes up 0.1 to 65% by weight relative to the total weight of the powder mixture

and which material is prepared by combining the substances 30-55% by weight CaO, 35-50% by weight P₂O₅, 1-20% by weight Na₂O, 0.5-20% by weight K₂O and 0.1-5% by weight MgO and optionally up to 5% by weight SiO₂, homogenizing and drying the mixture and subjecting it to a step-by-step thermal treatment lasting 1-2h at 350-450°C, 750-850°C and 950-1,050°C respectively, melting the mixture at between 1,550 and 1,650°C, holding it at the melting temperature for between 10 and 60 minutes and finally cooling the mixture in a spontaneous or temperature-controlled manner and grinding it.

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